AMENDMENTS

In the Specification:

Amend paragraphs [0006], [0008], [0028], [0030], [0032], [0033], [0035], [0037], [0040], [0041], [0051], [0063], [0075], [0101], [0103] and [0104] as follows:

[0006]

The present inventors have conducted intensive studies and found that the dielectric loss tangent of a polyimide film can be unprecedentedly lowered by forming a particular higher order structure, and that such polyimide film simultaneously has heat resistance, applicability to high frequency and flexibility, which resulted in the completion of the present invention.

Accordingly, the present invention provides the following.

(1) A polyimide film obtainable by reacting an aromatic diamine with an aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydride, which has a planar orientation coefficient of 0.79-0.89 as measured by the X-ray diffraction method, and a dielectric constant of 2.7-3.1 at 100 GHz as measured by a cavity resonance perturbation method.

(2) The polyimide film of paragraph (1) just above, having a dielectric loss tangent at 100 GHz of 0.0001-0.03 as measured by the cavity resonance perturbation method.

(3) The polyimide film of paragraph (1) or (2) just above, having dielectric constants of 2.7-3.1 at 1 GHz and 2.6-3.0 at 100 GHz, as measured by the cavity resonance perturbation method.

(4) The polyimide film of any of paragraphs (1) to (3) just above, which has a density of 1.47 g/cm^3 - 1.55 g/cm^3.

(5) A polyimide film obtainable by reacting an aromatic diamine with an aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydride, wherein the amount of water vaporized at a high temperature during heating at 500°C for 10 sec of the film immediately after helium purge at 170°C for 7 min and preliminary drying is not more than 5000 ppm.

(6) The polyimide film of any of paragraphs (1) to (5) just above, wherein the ratio ($\varepsilon_{65}/\varepsilon_D$) of the dielectric constant ε_{65} at 100 GHz of the film humidity-conditioned under the constant

temperature and humidity conditions of 20°C, 65% RH for 94 hr, as measured by a cavity resonance perturbation method, to the dielectric constant εD at 100 GHz of the film vacuum dried under the conditions of 120°C for 24 hr, as measured by a cavity resonance perturbation method, is within the range of 1.00-1.10.

(7) A polyimide film obtainable by reacting an aromatic diamine with an aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydride, wherein the absolute value of the difference between the surface planar orientation degree of one surface (surface A) and the surface planar orientation degree of the other surface (surface B) of the film is 0-2.

(8) The polyimide film of any of paragraphs (1) to (7) just above, wherein the surface planar orientation degree of a surface having a higher surface planar orientation degree is not more than 15.

(9) The polyimide film of any of paragraphs (1) to (8) just above, which has a curling degree of 0%-5%.

(10) The polyimide film of any of paragraphs (1) to (9) just above, wherein the aromatic diamine has a benzoxazole structure.

(11) A base substrate for printed wiring assemblies, which comprises the polyimide film of any of paragraphs (1) to (10) just above.

(12) A method of producing a polyimide film, which comprises reacting an aromatic diamine with an aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydride to give polyamide acid, casting a solution thereof on a support and drying the solution and the like to give a self-supporting polyimide precursor film (green film) and polyimidating said precursor film, wherein the polyimide precursor film (green film) satisfies all the relationships shown by the following formulas between an imidation rate Aim of one surface side (surface A side) and an imidation rate Bim of the other surface side (surface B side) of the polyimide precursor film (green film) and said polyimide precursor film is subjected to imidation.

   formula 1: $|Aim-Bim| \leq 5$

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formula 2: $0 \le Aim \le 15$

formula 3: $0 \le Bim \le 15$.

[0008]

The embodiment of the polyimide film of the present invention is explained in detail in the following.

The polyimide film of the present invention is made of polyimide obtainable by reacting aromatic diamines with aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydrides, and has a particular higher-order structure, particular dielectric property or a particular curling degree.

The aforementioned "reacting" includes first subjecting diamines and ~~tetracarbonic~~ tetracarboxylic acid anhydrides to an open ring polyaddition reaction in a solvent to give a polyamide acid solution, then forming a green film and the like as necessary from the polyamide acid solution and subjecting the film to dehydrocondensation (imidation).

[0028]

The ~~tetracarbonic~~ tetracarboxylic acid anhydrides to be used in the present invention are aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydrides. As the aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydrides, the following can be concretely mentioned.
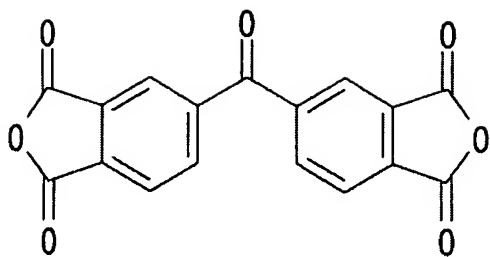
[0030][formula 15]

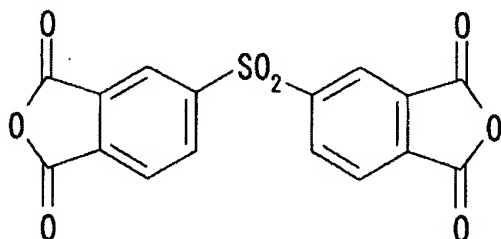3,3',4,4'-~~biphenyltetracarbonic~~ biphenyltetracarboxylic acid anhydride
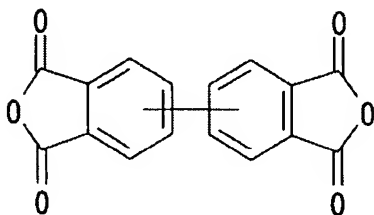
[0032][formula 17]

3,3',4,4'-~~benzophenonetetracarbonic~~ benzophenonetetracarboxylic acid anhydride

[0033][formula 18]

3,3',4,4'-~~diphenylsulfonetetracarbonic~~ <u>diphenylsulfonetetracarboxylic</u> acid anhydride

[0035]

The aromatic ~~tetracarbonic~~ <u>tetracarboxylic</u> acid anhydrides can be used alone or two or more kinds thereof can be used.

In the present invention, one or more kinds of the nonaromatic tetracarboxylic acid dianhydrides exemplified below may be concurrently used as long as their content is not more than 30 mol% of the total tetracarboxylic acid dianhydride. As the nonaromatic tetracarboxylic acid dianhydrides to be used, for example, butane-1,2,3,4-tetracarboxylic acid dianhydride, pentane-1,2,4,5-tetracarboxylic acid dianhydride, cyclobutanetetracarboxylic acid dianhydride, cyclopentane-1,2,3,4-tetracarboxylic acid dianhydride, cyclohexane-1,2,4,5-tetracarboxylic acid dianhydride, cyclohex-1-ene-2,3,5,6-tetracarboxylic acid dianhydride, 3-ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic acid dianhydride, 1-methyl-3-ethylcyclohexane-3-(1,2),5,6-tetracarboxylic acid dianhydride, 1-methyl-3-ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic acid dianhydride, 1-ethylcyclohexane-1-(1,2),3,4-tetracarboxylic acid dianhydride, 1-propylcyclohexane-1-(2,3),3,4-tetracarboxylic acid dianhydride, 1,3-dipropylcyclohexane-1-(2,3),3-(2,3)-tetracarboxylic acid dianhydride, dicyclohexyl-3,4,3',4'-tetracarboxylic acid

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dianhydride, bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic acid dianhydride, 1-propylcyclohexane-1-(2,3),3,4-tetracarboxylic acid dianhydride, 1,3-dipropylcyclohexane-1-(2,3),3-(2,3)-tetracarboxylic acid dianhydride, dicyclohexyl-3,4,3',4'-tetracarboxylic acid dianhydride, bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic acid dianhydride, bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic acid dianhydride, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride and the like can be mentioned.   The nonaromatic tetracarboxylic acid dianhydrides can be used alone or two or more kinds thereof can be used.

[0037]

The polyimide film of the present invention is produced by (a) first condensing aromatic diamines and aromatic ~~tetracarbonie~~ <u>tetracarboxylic</u> acid anhydrides in a solvent to give a polyamide acid solution (hereinafter to be referred to as Step (a)), then, (b) applying the polyamide acid solution to a support and drying the solution to afford self-supportiveness, which is specifically drying under the conditions to achieve the amount of the residual solvent relative to the total mass after drying of 25-50% by mass, to give a polyimide precursor film (also referred to as a green film) (hereinafter to be also referred to as step (b)), then, (c) heat treating the green film at a maximum temperature of 100-500°C to allow imidation reaction (hereinafter to be referred to as step (c)).

[0040]

Step (a)

The solvent used for polymerizing aromatic diamines and aromatic ~~tetracarbonie~~ <u>tetracarboxylic</u> acid anhydrides to give polyamide acid is not particularly limited as long as it can dissolve any of the monomers to be the starting materials and the resulting polyamide acid. Preferred are polar organic solvents and, for example, N-methyl-2-pyrrolidone, N-acetyl-2-pyrrolidone, N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, hexamethylphosphoric amide, ethyl cellosolveacetate, diethyleneglycoldimethylether, sulforane, halogenated phenols and the like can be mentioned.

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These solvents can be used alone or in a mixture. The amount of the solvent to be used is any as long as it is sufficient to dissolve monomers to be the starting materials. As a concrete amount to be used, an amount that affords generally 5-40% by mass, preferably 10-30% by mass, of the monomers in the solution dissolving the monomers can be mentioned.

[0041]

The conditions for the polymerization reaction (hereinafter to be also simply referred to as "polymerization reaction") to obtain polyamide acid may be conventionally known ones, and a specific example includes continuous stirring and/or mixing in an organic solvent within a temperature range of 0-80°C for 10 min - 80 hr. Where necessary, the polymerization reaction may be divided, pressure may be applied or the temperature may be increased or decreased. In this case, while the order of addition of both monomers is not particularly limited, addition of aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydrides to a solution of aromatic diamines is preferable. The mass of polyamide acid in the polyamide acid solution obtained by the polymerization reaction is preferably 5-40% by mass, more preferably 10-30% by mass, and the viscosity of the aforementioned solution is preferably 10-2000 Pa·s, more preferably 100-1000 Pa·s, as measured by a Brook Field viscometer (25°C) in view of feeding stability.

[0051]

The timing of the addition of a dehydrating agent to a polyamide acid solution is not particularly limited, and it may be added in advance before a polymerization reaction to obtain polyamide acid. Specific examples of the dehydrating agent include aliphatic ~~carbonic~~ carboxylic acid anhydrides such as acetic anhydride, propionic acid anhydride, butyric acid anhydride and the like, aromatic ~~carbonic~~ carboxylic acid anhydrides such as benzoic acid anhydride and the like, and the like. Of these, acetic anhydride, benzoic acid anhydride and a mixture thereof are preferable. While the amount of the dehydrating agent to be used is not particularly limited, it is preferably 0.1-4 mol per 1 mol of polyamide acid. When a dehydrating agent is used, a gelation retardant such as acetylacetone and the like may be used in combination.

[0063]

<Curling degree>

The polyimide film of the present invention is an about flat film made of polyimide obtained by polycondensation of aromatic diamines and aromatic ~~tetracarbonic~~ tetracarboxylic acid anhydrides, and preferably has a curling degree of not more than 5%. It is possible to have unprecedented superior thermal degradation stability. A concrete measurement operation of the curling degree of a film is described in the Examples.

[0075]

The effectiveness of the present invention is explained in the following by referring to Examples, which are not to be construed as limitative. In the following Examples, the evaluation methods of the properties are as follows.

1. Reduced viscosity (ηsp/C) of polyamide acid

A solution of a polymer in N-methyl-2-pyrrolidone to a polymer concentration of 0.2 g/dl was measured with a ~~Uberode~~ Ubbelohde type viscosity tube at 30°C.

2. Film thickness of polyimide film

The film thickness was measured with a micrometer (Millitron (R)1245D, manufactured by Finepruf).

3. Tensile elastic modulus, tensile strength at break and tensile elongation at break of polyimide film

A film after drying was cut out in the longitudinal direction (MD direction) and transverse direction (TD direction) to give a reed-shaped strip (length 100 mm, width 10 mm) as a test piece, which was subjected to the measurement of tensile elastic modulus, tensile strength at break and tensile elongation at break using a tensile test machine (AUTOGRAPH (R), model AG-5000A, manufactured by Shimadzu Corporation) at a tensile rate of 50 mm/min and a chuck distance of 40 mm.

[0101]

8.

(Examples 9-[[11]] 10, Comparative Examples 8-10)

In the same manner as in Example 7 except that the obtained green film was passed through a nitrogen purged continuous type heat treatment furnace, and heated in two steps under the conditions described in Table 4 to carry out an imidation reaction, a polyimide film was obtained and subjected to the evaluation in the same manner. The evaluation results are shown in Table 4.

[0103]

(Example [[12]] 11)

<Preparation Example of polyamide acid solution - 5>

A polyamide acid solution was obtained by a method similar to that in Example 7.

<Production Example of film - 5>

The polyamide acid solution was applied to a stainless belt (squeegee/belt gap was 650 μm) and dried in three hot air type drying zones at 90°C×20 min, 90°C×20 min and 90°C×20 min.

After drying, a self-supporting polyamide acid film was peeled off from a stainless belt to give a green film having a thickness of 40 μm. The obtained green film was passed through a continuous type drying furnace, and heat-treated at 170°C for 3 min, after which the temperature was elevated to 450°C over about 20 seconds, the film was heat-treated at 450°C for 7 min and cooled to room temperature over 5 min to give a brown polyimide film having a thickness of 25 μm. The properties of the obtained polyimide film are shown in Table 5.

[0104]

(Examples ~~13, 14~~ 12, 13, Comparative Examples 11-14)

In the same manner as in Example [[12]] 11 except that a polyamide acid solution was applied to a stainless belt and temperature×time of the three hot air type drying zones was as shown in Table 5, a green film was obtained, which was then heat treated in the same manner as in Example [[12]] 11 to give a polyimide film.

The property values of the polyimide films of Examples ~~13 and 14~~ <u>12 and 13</u> are shown in Table 5, and the property values of the polyimide films of Comparative Examples 11-14 are shown in Table 6.

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